

VI.1 Proton Conducting Solid Oxide Fuel Cell

Objectives

- Identification of dopant type and concentration in a perovskite host to achieve high proton conductivity and high protonic transference number under SOFC operating conditions.
- Selection of dopant type and concentration in a perovskite host to provide resistance to reactivity towards CO_2 and H_2O .
- Evaluation of electrode materials using symmetric cells and full cells in button cell configuration.
- Test button cells using syngas as fuel for cell performance and endurance.

Approach

- Select an appropriate B-site dopant in a perovskite matrix by evaluating protonic conductivity and transference number in SOFC relevant atmospheres.
- Investigate stability of compositions in syngas.
- Select a composition and evaluate in button cell tests.

Accomplishments

- The project is in the initial stages of compositional evaluation.

Future Directions

- Selection and verification of compositions for high protonic conductivity, transference number, and stability in syngas.
- Evaluation of performance in button cell tests.

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Introduction

One of the prime attractions of fuel cells is the possibility of realizing energy conversion efficiencies much higher than possible with the thermal cycle systems. The basis of this difference is that thermal cycle system efficiencies are bounded by Carnot cycle thermodynamics, whereas fuel cell efficiencies are determined by chemical equilibrium thermodynamics and non-equilibrium force-flux relationships that govern charge, mass, momentum and energy transport. Materials have been developed which function as high temperature solid electrolytes in fuel cell applications. Two of the most widely considered materials are yttria stabilized ZrO_2 (YSZ) which transports oxygen ions and gadolinium doped BaCeO_3 which transports protons [1].

The thermodynamic difference between proton and oxygen ion cells is manifest in reversible potential variation with reactant utilization as a function of product water location. Excess air flow, used to remove the heat generated by cell operation, results in a lower water concentration in the cathode stream of a proton cell than in the anode stream of an O^{2-} cell.

Reversible potential variation with fuel utilization is shown for both proton and oxygen ion cells in Figure 1. The proton cell has a substantially higher reversible potential across the full range of fuel utilization. An interesting observation is that steam ratios greater than stoichiometric ($\text{S}/\text{C}=2$) increase the high utilization potential of a proton cell while oxygen ion cell potentials are uniformly higher with sub-stoichiometric steam ratios. This is due to the use of carbon monoxide via

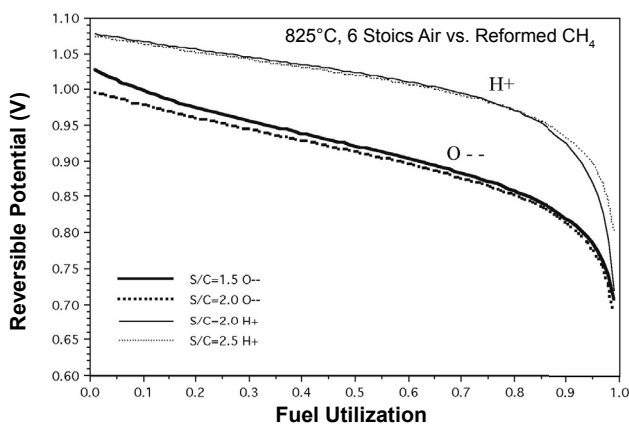


FIGURE 1. Comparison of Reversible Cell Potential

the shift reaction. The oxygen ion cell generates water in the anode stream so inlet compositions can be water deficit (high potential) and still have sufficient water to drive the shift reaction as utilization increases. The proton cell, on the other hand, must have sufficient or even excess water at the inlet to drive the shift reaction at high utilizations. However, water in the anode stream does not directly enter in the calculation of proton cell potentials and thus has little effect on the potential until higher utilizations where shift produced hydrogen is important. Thus, high temperature proton conductors have a thermodynamic advantage over oxygen ion conductors.

Comparable electrolyte ionic conductivities are required to take practical advantage of the thermodynamic benefit. Applications driven by maximizing efficiency at the expense of power density would favor proton cells. Thus, the opportunity for very high efficiency operation is one of the primary motivating factors for investigating proton conducting solid oxide fuel cells (P-SOFC). However, to date the research work on P-SOFC has lagged far behind the well-known YSZ-based oxygen conducting solid oxide fuel cells (O-SOFC). The challenges that have been encountered in P-SOFC systems are discussed below.

Proton Conductivity

As mentioned earlier, the differences in electrolyte ionic conductivity may be greater than differences in driving force and must be included in any comparison of an operating cell at a fixed current density. In general, the protonic conductivity of commonly known perovskite materials such as doped SrCeO_3 and BaCeO_3 are considerably lower than the oxygen ion conductivity of YSZ. The proton conductivity ranges from 5×10^{-5} to $2 \times 10^{-2} \text{ S/cm}$ at 800°C [2,3,4,5,6]. While the high end of this range is comparable to the oxygen conductivity of 8-YSZ, the perovskite materials also possess some level of oxygen ion conductivity and electronic conductivity at various temperatures. Thus, the protonic transference number varies as a function of temperature. While the doped BaCeO_3 composition functions as an effective electrolyte, an increase in hydrogen conductivity is preferable to fully exploit the benefit of high efficiency with high power density.

Stability

One of the biggest technical challenges lies in maintaining the chemical stability of the perovskite in the presence of CO_2 and moisture; both are present in a typical hydrocarbon fuel. Numerous studies have confirmed the instability of the perovskite compositions.

It has been shown [7] that partial replacement of the B-site dopant with Zr completely eliminates this reaction. A similar improvement in stability in moist

conditions was also reported with Zr substitution [8]. However, the stability improvement is at the expense of protonic conductivity. The proton conductivity was found to decrease monotonically with increasing Zr content [9,10,11].

Thus, what is required for successful development of a P-SOFC is an electrolyte material that has high proton conductivity to achieve a low area specific resistance, high protonic transference number relative to oxygen transference number to realize high efficiency, and stability in CO_2 and H_2O without compromising protonic conductivity for cell operation using practical hydrocarbon fuels.

Approach

Perovskite compositions that are known to exhibit protonic conductivity will be evaluated for dopant study. The B-site dopants, typically rare earth metals, have been shown to increase the proton conductivity of perovskites such as BaCeO_3 . Several dopants and dopant levels will be screened to identify compositions that have high conductivity and stability. The best composition will be evaluated in button cell tests using hydrogen and syngas fuels.

Results

Materials synthesis is in progress.

References

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